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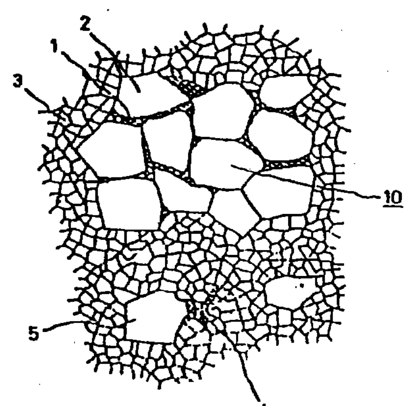
(54) High toughness ceramics and process for the preparation thereof.

(57) The present invention relates to a sintered product containing silicon carbide as a main component which comprises a phase (a) containing at least one metal selected from among Al, Sc, Y and rare earth elements and oxygen, a particle phase (b) comprising at least one metal carbide selected from among carbides of Ti, Zr, Hf, Va, Nb, Ta, W and the like, a composite particle phase (c) comprising said phase (a) and said phase (b) surrounding the phase (a) and silicon carbide matrix (d) in which the above phase (a), (b) and (c) are dispersed.

The silicon carbide sintered product of the present invention exhibits a remarkably high strength and a remarkably high toughness which have not been attained up to this time, so that it can form various heat-resistant structural materials having a high reliability.

FIG. 1



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HIGH TOUGHNESS CERAMICS AND PROCESS FOR THE PREPARATION THEREOF

The present invention relates to ceramics. Particularly it relates to a toughened silicon carbide material which may be useful as a structural material.

A silicon carbide material may have a high heat resistance, a high oxidation resistance and an excellent high-temperature strength, so that it is expected to be widely used as a heat-resistant structural material. However, known sintered silicon carbide is fragile (i.e. the toughness is low), so that it has only a low reliability as a structural material, which is the greatest barrier for the practical use of silicon carbide ceramics.

To overcome this disadvantage, it was reported in, for example, Journal of the American Ceramic Society, 67, 571 (1984) that titanium carbide particles may be dispersed in silicon carbide matrix to thereby prevent the propagation of crack in a sintered body thus improving the toughness. However, the sintered material obtained by this method has a structure where

titanium carbide particles are only dispersed in silicon carbide matrix and exhibits a fracture toughness of at most $6MN/m^{3/2}$, so that it can not be used without anxiety as a structural material which requires a high reliability.

Embodiments of the present invention may provide silicon carbide ceramics having a high reliability, being tough enough to be used as structural materials for various purposes.

The present invention provides silicon carbide sintered materials having a structure where a phase (a) comprising at least one metallic element selected from aluminum, scandium, yttrium and rare earth elements, and oxygen; a particle phase(b) comprising at least one metal carbide other than silicon carbide, such as titanium, zirconium, hafnium, vanadium, niobium, tantalum or wolfram (tungsten) carbide; and a composite particle phase(c) comprising such a phase(a) and such a particle phase(b) surrounding the phase(a) are dispersed in a matrix(d) comprising silicon carbide.

As described above, the particle phase(b) is formed around the phase(a) in the sintered silicon carbide of the present invention. In other words, the sintered silicon carbide of the present invention has a structure

where the composite particle phases(c) have a structure where the grain boundary between the metal carbide particle phases(b) is filled with the phase (a), that is to say, the particle phases (b) are bonded with each other via the phase (a); and these composite phases (c) are dispersed in a matrix (d) comprising silicon carbide. It has been found that the presence of the above structure remarkably enhances the fracture toughness of a sintered silicon carbide.

Fig. 1 shows schematically a structure of an embodiment of the high toughness ceramic of the present invention. In this figure, numeral 1 refers to a phase (a) containing at least one metallic element selected from among aluminum, scandium, yttrium and rare earth elements and oxygen, the metals being generally present as an oxide. 2 is a metal carbide particle phase(b) surrounding the phase(a) and forms a composite particle phase (c) 10 together with the phase(a).

The phase(b)-constituting metal carbide must have a high melting point and be stable in silicon carbide and is preferably at least one carbide selected from among titanium, zirconium, hafnium, vanadium, niobium, tantalum and wolfram carbides. Among them, titanium or vanadium

carbide or a mixture thereof are particularly preferred as a particle phase(b)-constituting metal carbide, because they are relatively light, exhibit a relatively high oxidation resistance at a high temperature and are particularly effective in enhancing the toughness of sintered silicon carbide. 3 is a silicon carbide particle which is a main component of the high toughness ceramic of the present invention and forms a matrix(d), in which the above phases are dispersed.

4 and 5 are phases comprising the same components as the ones of phase 1 and 2, respectively. That is to say, 4 and 5 show the phases(a) and (b) which are alone dispersed in the silicon carbide matrix (d).

As described above, a high toughness ceramic having a high reliability can be obtained for the first time by dispersing composite particle phases(10) having a structure where phases(1) comprising a metallic element selected from among aluminum, scandium, yttrium and rare earth elements and oxygen are present among metal carbide particles(2) to bond the particles(2) with each other via phase(1) in a silicon carbide matrix.

The reasons why the ceramic of the present invention exhibits an improved toughness are thought to be the branching and termination of crack. That is to say, the difference in thermal expansion coefficient and

Young's modulus between the silicon carbide particles of the matrix and the composite particle phase causes stress around and in the composite particle phase. Crack propagating in the ceramic is deflected by this stress to be taken into the composite particle. Then, the crack generally branches, propagates on the interface between the phases(a) and (b) and is terminated in the composite particles. In some cases, the crack propagates inside of the phase(b) and deflects in the direction of cleavage of the metal carbide particle and is terminated also in the composite particle. As described above, the composite particle acts as a crack energy absorber, so that crack propagation becomes too difficult in the ceramic, thus enhancing the toughness.

The high toughness ceramic of the present invention can be prepared by adding at least one metal or its compound selected from among aluminum, scandium, yttrium ,rare earth elements and hydride, carbide, nitride, silicide and oxide thereof, and a metal (for example, titanium, zirconium, hafnium, vanadium, niobium, tantalum or wolfram) or alloy, hydride, nitride or silicide thereof which can form a carbide in silicon carbide to silicon carbide powders and by firing the mixture at 1900 to 2300°C either under vacuum or in an inert atmosphere.

In the firing step, a metal selected from among aluminum, scandium, yttrium and rare earth elements or a compound thereof acts as a sintering aid to give a dense sintered product. At the same time, the metals or metal compounds other than oxides react with oxygen or surface oxide film adhering to the surface of silicon carbide particle or oxygen or surface oxide film adhering to the added particle of titanium, zirconium, hafnium, vanadium, niobium, tantalum, wolfram or the like to form an oxide, thus forming an oxide phase of aluminum, scandium, yttrium or rare earth elements in the sintered product.

The average particle size of the silicon carbide to be used as a raw material is preferably from 0.1 to 2μm. If the particle size is less than 0.1μm, the handling of the raw material become difficult and a homogeneous sintered product may not result. If it is more than 2μm, the dense sintering is difficult and a sintered product having a high density and a high strength may not result.

Preferred examples of the sintering aid include metallic aluminum and aluminum carbide, nitride and oxide and metallic yttrium and yttrium hydride. The use of these sintering aids can give a dense sintered product. When a sintering aid containing yttrium is

used, the generated yttrium oxide(Y_2O_3) has a high melting point of 2410°C, so that the obtained high toughness ceramic is advantageous in that the mechanical properties do not change until a high temperature. In this connection, melting points are Al_2O_3: 2054°C, La_2O_3: 2307°C, CeO_2: 1950°C.

Further, in the firing step, a metal such as titanium, zirconium, hafnium, vanadium, niobium, tantalum, wolfram or a compound thereof such as hydride, nitride or silicide is reacted with silicon carbide to be converted into the corresponding carbide. At the same time, an aggregate structure of the carbide particles is formed, thus forming the above-described composite particle phase(c) which is effective in enhancing the toughness. In some cases, the silicon generated by this reaction is taken into the phase(a) comprising an oxide of aluminum, scandium, yttrium or rare earth metal and is present in the phase(a) as a simple substance, silicate or silicate glass under certain conditions.

As described above, the composition of the phase(a) varies depending upon the kind of the raw materials used or the sintering conditions, and can be selected from among Al_2O_3, Y_2O_3, La_2O_3, CeO_2, $Y_4Al_2O_3$, Al_2SiO_5, Y_2SiO_5, alumino silicate glass, yttrium-silicate glass, for example. A silicate of the specified metal(s) may be its main component, e.g. as a glass.

In the above case, where the phase(a) contains silicon, even if all of the phases(a) and (b) are homogeneously dispersed in the silicon carbide matrix(d), so that the above-described composite particle phase(c) is not formed, the enhancement in the toughness of the sintered product is observed, though slightly lower than that the case where the phase(c) is formed.

It is preferred that the above composite particle(c) has a diameter of about 30 to 150μm. If the diameter is less than 30μm, the particle is only slightly effective in preventing crack propagation. On the contrary,if the composite particle is too large, the difference in thermal expansion coefficient between the silicon carbide matrix and the composite particle causes cracks and these cracks become defects, thus decreasing the strength of the sintered product. Furthermore to prepare a ceramic having a sufficiently high strengh and a sufficiently high toughness, it is preferred that at least 50% by volume of the total composite particles has a diameter of 30 to 150μm.

To form the above composite particle, it is preferred that the metal, alloy or metal hydride to be used as a raw material for the phase(b) has an average particle size of 5 to 100μm. Such a material is reated with silicon carbide during sintering to form a

fine metal carbide particle and this particle forms the composite particle phase(c) effective in enhancing the toughness together with the phase(a) containing a sintering aid as a main component. If the particle size of the metal, alloy or hydride to be used as a raw material is too small or too large, the formation of the composite particle having a diameter of 30 to 150µm is difficult.

Further, it is preferred that the metal carbide particle phase(b) which constitutes the composite particle phase(c) has an average particle size of 1 to 20µm. If the metal carbide particle is too small, it will not be effective in terminating crack, while if it is too large, it will not be effective in branching crack.

The amount of the phase (a) is preferably 0.05 to 10% by volume. If the amount is too small, a sufficiently dense sintered product may not result and the bonding of the composite particle(c)-constituting metal carbide particles(b) with each other becomes weak. If the amount is too large, the excellent characteristics inherent to silicon carbide may be lost or impaired.

The amount of the composite particle(c) as calculated from an area ratio of the section of the sintered product is preferably from 5 to 30% by volume.

The amount of the metal carbide present in the

sintered product is preferably 5 to 40% by volume. If the amount is too small, the toughness is not sufficiently improved, while if it is too large, the excellent properties inherent to silicon carbide are lost or impaired.

It is preferred that a ceramic to be used as a structural material requiring a high reliability, such as a turbocharger rotor or a gas turbine rotor, has a toughness of $10MN/m^{3/2}$ or above in terms of critical stress intensity factor K_{IC}. The ceramic of the present invention may exhibit a strength of $30kg/mm^2$ or above, even if defects of about 100μm are present on the surface of the ceramic or within the ceramic, thus satisfying the tolerance strength for design of the above rotors. Defects having a size of more than 100μm which are present in the ceramic can be non-destructively found by X-ray penetration method, supersonic flaw detection method, viewing method or the like and can be removed.

The use of a ceramic having a K_{IC} of $10MN/m^{3/2}$ or above can prevent the breakage caused by very small, unavoidable internal defects or surface flaws. Much energy is required for crack to grow in a ceramic having a high K_{IC}, therefore preventing the growth of the crack, which is thought to be the reason why the characteristics

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of the ceramic are stable and highly reliable for a long period.

The high toughness ceramic of the present invention may have a high K_{IC} of more than $10MN/m^{3/2}$, when it contains the phase(a) in an amount of 0.05 to 10% by volume and the composite particle phase(c) in an amount of 5 to 30% by volume. The growth of cracks in a ceramic having such a high K_{IC} requires 3 to 10 times as much energy as that required in a ceramic of the prior art having a K_{IC} of about 3 to $6MN/m^{3/2}$, so that the ceramic having such a high K_{IC} becomes more reliable as a structural material. It is preferred that the particle size of the particle phase(b) is larger than that of the SiC matrix(d).

Brief Description of the Drawings:-

Fig. 1 is a schematic view of a structure of a high toughness ceramic embodying the invention. Fig. 2 shows a cross-section of a piping valve for atomic energy plant which is an example of the use of such materials.

The present invention will be exemplified in the following Examples, but is not limited by them.

Example 1

A hydride YH_x (wherein x is 1 or 2) having an average particle size of 0.7μm or a metal Y having an

average particle size of 3μm and a carbide-formable metal or hydride thereof having a particle size of 5 to 100μm, which will be shown in Table 1, were added to α-type of SiC powder having an average particle size of 0.5μm, in an amount of 3 to 70% by volume in terms of metal carbide, followed by mixing. 5% by volume of a silicone resin was added as a binder to the obtained powdery mixture. The obtained mixture was passed through a 16-mesh screen and granulated. The resulting granulated mixture was placed in a metal mold and molded under a pressure of 500kg/cm^2 into a circular plate having a diameter of 60mm and a thickness of 10mm. The molded product was placed in a mold made of graphite and hot-pressed by induction heating under vacuum. The hot pressing was carried out under a pressure of 300kg/cm^2 and according to a temperature profile which comprises heating at a heating rate of 20 to 40°C/minute to a temperature of 2000 to 2200°C and cooling immediately at the same rate.

A column sample (3mm X 4mm X 45mm) was prepared from the obtained sintered product and examined for strength according to JIS three-point bending test (with a span of 30 mm). The bending strength at 1200°C under vacuum, the bending strength at the same temperature after the treatment at 1000°C in air for 1000 hours and the bending strength after giving a

Vickers indentation flaw on the surface of the sample with a load of 20 to 50kg were measured. The fracture toughness (critical stress intensity factor K_{IC}) calculated from the area of Vickers indentation flaw and the bending strength is shown in Table 1. The K_{IC} values were calculated according to the following equation:

$$K_{IC} = \frac{1}{0.84} \cdot \sigma \cdot s^{1/4}$$

wherein σ is bending strength and s is area of indentation flaw.

The X-ray diffraction analysis of the samples shown in Table 1 showed that all of the added YH_x were present as Y_2O_3 in the sintered product, while all of the carbide-formable metals were present as metal carbide. In the sintered product obtained under the above conditions, 30 to 70% of the Y_2O_3 was present in the grain boundary of the composite particle phase(c) and about 50 to 75% of the metal carbide was dispersed as a sole particle, while the balance, i.e. about 25 to 50%, of the metal carbide was dispersed as an aggregate of the particles among which Y_2O_3 phase was present, thus forming the composite particle phase(c). Further, the X-ray microanalysis of the Y_2O_3 phase of the sample obtained by using Ti as a carbide-formable metal showed that the Y_2O_3 phase contained not only Y and O

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but also Si and that Y_2SiO_5 was present in the phase. This Si is thought to be generated by the reaction between Ti and SiC.

The raw material having the same composition as the one of the sample shown in Table 1 was sintered at a hot pressing temperature of 2200°C with a retention time of 2 hours to obtain a sample. In this sample, all of the carbide-formable metal was converted into the corresponding metal carbide, about 50% of which was dispersed as an aggregate thereof. However, no Y_2O_3 phase was present among the metal carbide particles in the sample and the sample exhibited a K_{IC} of 3 to $4MN/m^{3/2}$ which is about equal to that of the sintered silicon carbide of the prior art, which may be probably because Y_2O_3 was evaporated during the holding of 2 hours at 2200°C. It seems necessary that the mixture of raw materials is immediately cooled to lower the temperature after sintering, though the condition may be varied depending upon the kind of the additive. However, rapid cooling may cause breakage.

Table 1 (1)

No.	Phase(a) in sintered product: Additive	Phase(a) in sintered product: Phase(a)	Phase(a) in sintered product: Amt. of phase(a) (Vol %)	Phase(c) in sintered product: Additive	Phase(c) in sintered product: Phase(b)	Phase(c) in sintered product: Amt. of phase(c) (Vol %)	Bending strength at 1200°C (MPa)	Bending strength after the treatment at 1000°C for 1000 hr (MPa)	K_{IC} $(MN/m^{3/2})$
1	YHx	Y_2O_3	0.02	VH_2	VC	15	720	700	8
2	"	"	0.05	"	"	"	1050	1040	12
3	"	"	2	"	"	"	1200	1150	15
4	"	"	5	"	"	"	1250	1200	16
5	"	"	10	"	"	"	1100	1010	14
6	"	"	15	"	"	"	610	600	9
7	"	"	5	"	"	2	1100	1100	7
8	"	"	"	"	"	5	1270	1250	13
9	"	"	"	"	"	10	1250	1230	16
10	"	"	"	"	"	30	1000	910	16
11	"	"	"	"	"	50	400	150	14
12	"	"	0.05	"	"	5	1000	1010	12
13	"	"	10	"	"	30	1100	990	16
14	"	Y_2SiO_5	0.02	Ti	TiC	15	500	480	7
15	"	"	0.05	"	"	"	760	740	11
16	"	"	2	"	"	"	850	810	15
17	"	"	5	"	"	"	900	850	16

Table 1 (2)

No.	Phase(a) in sintered product			Phase(c) in sintered product			Bending strength at 1200°C (MPa)	Bending strength after the treatment at 1000°C for 1000 hr (MPa)	K_{IC} ($MN/m^{3/2}$)
	Additive	Phase(a)	Amt. of phase(a) (Vol %)	Additive	Phase(b)	Amt. of phase(c) (Vol %)			
18	YHx	Y_2SiO_5	10	Ti	TiC	15	810	800	15
19	"	"	15	"	"	"	400	380	11
20	"	"	5	"	"	2	700	700	8
21	"	"	"	"	"	5	830	800	12
22	"	"	"	"	"	10	910	900	16
23	"	"	"	"	"	30	750	610	17
24	"	"	"	"	"	50	320	140	15
25	"	Y_2O_3	0.05	Zr	ZrC	5	1020	820	10
26	"	"	5	"	"	15	1100	510	11
27	"	"	10	"	"	30	1000	-*	11
28	Y	Y_2O_3	0.05	Hf	HfC	5	980	800	10
29	"	"	5	"	"	15	1050	620	11
30	"	"	10	"	"	30	1010	-*	10
31	"	"	0.05	Nb	NbC	5	1100	910	10
32	"	"	5	"	"	15	1210	480	12
33	"	"	10	"	"	30	1030	-*	12
34	"	"	0.05	TaH_2	TaC	5	1000	850	11
35	"	"	5	"	"	15	1050	500	11
36	"	"	10	"	"	30	1050	-*	10
37	"	"	0.02	W	WC, W_2C	15	680	310	8
38	"	"	0.05	"	"	"	970	420	12
39	"	"	2	"	"	"	1020	450	15

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Table 1 (3)

No.	Phase(a) in sintered product			Phase(c) in sintered product			Bending strength at 1200°C (MPa)	Bending strength after the treatment at 1000°C for 1000 hr (MPa)	K_{IC} ($MN/m^{3/2}$)
	Additive	Phase(a)	Amt. of phase(a) (Vol %)	Additive	Phase(b)	Amt. of phase(c) (Vol %)			
40	Y	Y_2O_3	5	W	WC, W_2C	15	1100	500	15
41	"	"	10	"	"	"	1010	480	16
42	"	"	15	"	"	"	500	380	13
43	"	"	5	"	"	2	1050	920	7
44	"	"	"	"	"	5	1100	1010	11
45	"	"	"	"	"	10	1110	800	15
46	"	"	"	"	"	30	980	-*	16
47	"	"	"	"	"	50	420	-*	14

* decomp.

It is apparent from Table 1 that a ceramic exhibits a high K_{IC} and a high bending strength, particularly when it contains 0.05 to 10% by volume of the Y_2O_3 phase(a) and 5 to 30% by volume of the composite particle phase(c), which are calculated from the area ratio of the section. Particularly, a ceramic having a bending strength at 1200°C of 400MPa or above and a K_{IC} 10MN/mm$^{3/2}$ or above can be obtained.

The samples Nos. 10 and 12 shown in Table 1 were examined for their structure. This examination showed that the total amounts of VC present in the sintered products were 40 and 7% by volume, respectively, about 75% of which was present as the composite particle and that both had particle sizes of VC of 5 to 20μm, while those of the composite particle varied widely over the range of 10 to 150μm and 70% of the composite particle had a particle size of 30 to 150μm.

The sample No. 16 shown in Table 1 was examined in a similar manner as above. The total amount of TiC present in the sintered product was 20% by volume, 75% of which was present as the composite particle. The particle size of TiC which was the phase(b) was 1 to 10μm. The size of the composite particle(c) varied over the range of 3 to 100μm and 50% of the particle(c)

had a size of 30 to 100μm.

Example 2

A mixture of SiC having a particle size of 0.5 to 1.0μm and additives having a particle size of 0.7 to 100μm was treated according to the same procedure as the one described in Example 1 to prepare a sample shown in Table 2. These samples were examined for characteristics. In these samples, all of the added sintering aid was present as an oxide in the sintered product, about 30 to 70% of which was present in the grain boundary of the composite particle phase(c) as the phase(a). All of the added carbide-formable metal was present in the sintered product as a metal carbide, 25 to 75% of which formed the composite particle phase(c).

Table 2 (1)

No.	Phase(a) in sintered product			Phase(c) in sintered product			Bending strength at 1200°C (MPa)	Bending strength after the treatment at 1000°C for 1000 hr (MPa)	K_{IC} $(MN/m^{3/2})$
	Additive	Phase(a)	Amt. of phase(a) (Vol %)	Additive	Phase(b)	Amt. of phase(c) (Vol %)			
1	Aℓ	A $_2O_3$	0.05	V	VC	5	620	600	13
2	"	"	5	"	"	15	800	800	15
3	"	"	10	"	"	30	840	820	15
4	AℓN	"	0.05	"	"	5	700	700	14
5	"	"	5	"	"	15	900	890	17
6	"	"	10	"	"	30	850	790	16
7	$Aℓ_2O_3$	"	0.02	VH_2	"	2	400	380	9
8	"	"	0.05	"	"	5	770	750	11
9	"	"	5	"	"	15	810	780	15
10	"	"	10	"	"	30	720	570	15
11	"	"	15	"	"	50	230	110	13
12	"	$Aℓ_2SiO_5$	10	Ti	TiC	5	680	650	15
13	"	"	"	"	"	30	610	500	14
14	"	"	0.05	"	"	"	570	500	14
15	"	"	"	"	"	5	520	510	13
16	"	"	0.02	"	"	50	310	160	8
17	Sc_2O_3	Sc_2O_3	0.05	"	"	5	530	520	10
18	"	"	5	"	"	15	550	530	12
19	"	"	10	"	"	30	500	380	11
20	Y_2O_3	Y_2SiO_5	0.05	"	"	30	600	410	15
21	"	"	5	"	"	15	680	610	16
22	"	"	10	"	"	5	730	730	15
23	LaH_3	La_2O_3	0.05	"	"	5	510	500	11

Table 2 (2)

No.	Phase(a) in sintered product			Phase(c) in sintered product			Bending strength at 1200°C (MPa)	Bending strength after the treatment at 1000°C for 1000 hr (MPa)	K_{IC} ($MN/m^{3/2}$)
	Additive	Phase(a)	Amt. of phase(a) (Vol %)	Additive	Phase(b)	Amt. of phase(c) (Vol %)			
24	LaH_3	La_2O_3	5	Ti	TiC	15	600	600	11
25	"	"	10	"	"	30	490	380	10
26	"	La_2SiO_5	0.05	WSi_2	WC, W_2C	5	400	270	10
27	"	"	5	"	"	15	450	330	11
28	LaH_3	La_2SiO_5	10	"	"	30	370	-*	11
29	LaC_2	La_2O_3	0.02	TaN	TaC	15	270	120	8
30	"	"	0.05	"	"	15	440	210	12
31	"	"	10	"	"	15	530	330	11
32	La_2O_3	"	15	VN	VC	5	430	420	10
33	"	"	10	"	"	30	620	400	10
34	"	"	5	"	"	50	310	180	7
35	$LaSi_2$	La_2SiO_5 glass	0.02	TiH_2	TiC	2	420	420	8
36	"	"	0.05	"	"	5	500	510	10
37	"	"	5	"	"	15	520	490	11
38	"	"	10	"	"	30	490	400	12
39	"	"	15	"	"	50	330	190	12
40	CeH_2	CeO_2	0.05	VH_2	VC	5	540	530	10
41	"	"	5	"	"	15	650	620	10
42	"	"	10	"	"	30	500	370	11
43	Y_5Si_3	Y_2SiO_5 glass	0.05	Ti	TiC	5	600	600	13
44	"	"	5	"	"	15	670	650	15

Table 2 (3)

No.	Phase(a) in sintered product			Phase(c) in sintered product			Bending Strength at 1200°C (MPa)	Bending strength after the treatment at 1000°C for 1000 hr (MPa)	K_{IC} ($MN/m^{3/2}$)
	Additive	Phase(a)	Amt. of phase(a) (Vol %)	Additive	Phase(b)	Amt. of phase(c) (Vol %)			
45	Y_5Si_3	Y_2SiO_5 glass	10	Ti	TiC	30	640	570	16
46	Al_5Si_3	Al_2SiO_5 glass	10	"	"	5	520	530	16
47	"	"	5	"	"	15	570	550	15
48	"	"	0.05	"	"	30	500	400	12
49	Y+Al (2:1)	$Y_4Al_2O_9$	0.05	VH_2	VC	5	1010	1000	14
50	"	"	5	"	"	15	1210	1200	16
51	"	"	10	"	"	30	1070	880	16
52	YH_2	Y_2O_3	0.05	V+Ti(1:1)	VC+TiC	5	1100	1050	13
53	"	"	5	"	"	15	1270	1180	15
54	"	"	10	"	"	30	1230	990	16

* decomp.

The sample No. 1 shown in Table 2 was examined for structure. The total amount of VC present in the sintered product was 5.5% by volume, about 90% of which was present as the composite particle (c). The particle size of VC was 1 to 20μm and the size of the composite particle varied over the range of 3 to 150μm, while 50% of the composite particle had a particle size of 30 to 150μm.

The sample No. 14 shown in Table 2 was examined in a similar manner as above. The total amount of TiC present in the sintered product was 40% by volume, about 75% of which was present as the composite particle (c). The particle size of TiC was 7 to 20μm. The size of the composite particle varied over the range of 20 to 200μm, while about 90% of the composite particle had a size of 30 to 150μm.

Particularly, a sintered product having a K_{IC} of $10MN/mm^{3/2}$ or above and a bending strength at 1200°C of 400MPa or above, can be obtained.

Example 3

60% by volume of a silicon carbide powder having an average particle size of 0.5μm, 15% by volume of a titanium carbide powder having an average particle size of 2μm, 23% by volume (in terms of the amount in the inorganic substance comprising silicon carbide as a main

component obtained by firing) of a polycarbosilane having a number-average molecular weight of 1850 which is solid at a room temperature and 2% by volume of an aluminum nitride powder as a sintering aid were mixed in an attritor. Xylene was added to the obtained powder in an amount of 10 to 15ml per 50g of the powder, followed by mixing. The obtained powdery mixture was granulated and molded in a metal mold. The obtained molded product was heat-treated in air at 350°C for 3 hours, held at 2050°C for 30 min and hot-pressed under a pressure of 30MPa under vacuum.

The surface of the obtained sintered product was subjected to mirror polishing and etched, followed by the observation of the microstructure thereof. A phase in which Al, Si and O were detectable with a wavelength dispersion X-ray analyzer was present among crystalline particles of silicon carbide and titanium carbide. The Si contained in this phase is thought to be generated during the pyrolysis of the polycarbosilane. Further, the titanium carbide particle phase(b) was not agglomerated but dispersed uniformly.

The sintered product exhibited a bending strength of 540 MPa at 1200°C under vacuum and a bending strength of 510MPa at the same temperature after the treatment at 1000°C for 1000 hr in an air and had a K_{IC} of $8MN/m^{3/2}$

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As described above, the high toughness ceramic of the present invention has a high fracture energy, so that it is highly resistant against mechanical and heat-shock. Therefore, the ceramic of the present invention can be used as gas turbine components (nozzle or rotor), turbocharger rotor, ball bearing, cutting machine (cutting tool or saw), piping valve which operates with a high shock or the like.

Fig. 2 shows a case where the high toughness ceramic of the present invention is used as the disc head of a piping valve for atomic energy plant (section) which requires wear resistance and shock resistance.

In Fig. 2, the ceramic of the present invention was applied to a disc head 11 which requires the highest strength in a piping valve for such plant, comprising a disc head 11, a disc 12, a cylinder 13, a shaft 14, a bonnet 15 and a pipe 16, thus obtaining a piping valve having a longer life and a higher operating reliability as compared with piping valves of the prior art.

As described above, the ceramic of the present invention has a remarkably high toughness and can be therefore used as a structural material, particularly as a component of an apparatus requiring a heat resistance and a high strength.

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CLAIMS:

1. A high toughness ceramic which comprises a silicon carbide matrix (d) in which are dispersed a phase (a) containing at least one metal selected from aluminum, scandium, yttrium and rare earth elements, and oxygen; and a particle phase (b) comprising at least one metal carbide other than silicon carbide, said phases (a) and (b) optionally and/or additionally being present as a composite particle phase (c) comprising said phase (a) and said particle phase (b) surrounding the phase (a).

2. A high toughness ceramic as set forth in claim 1, wherein the phase (a) contains silicon.

3. A high toughness ceramic as set forth in claim 2, wherein the phase (a) contains a silicate of at least one metal selected from the group consisting of aluminum, scandium, yttrium and rare earth elements as a main component.

4. A high toughness ceramic as set forth in claim 3, wherein the particle phase (a) contains a silicate glass as a main component.

5. A high toughness ceramic as set forth in any preceding claim, wherein the particle phase (b) has an average particle size of 1 to 20μm.

6. A high toughness ceramic as set forth in any preceding claim, wherein the silicon carbide matrix (d) has an average particle size of 0.2 to 5μm.

7. A high toughness ceramic as set forth in any prece-

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ding claim, wherein the composite particle phase (c) is present in an amount of 5 to 30% by volume in the ceramic.

8. A high toughness ceramic as set forth in any preceding claim, wherein composite particle phase (c) with an average particle size of 30 to 150μm is present in an amount of at least 50% by volume of total amount of a particle phase (b).

9. A high toughness ceramic as set forth in any preceding claim, wherein the composite particle phase (c) is present in an amount of 5 to 30% by volume in the ceramic; and at least 50% by volume of the total amount of particle phase (b) is present as composite particle phase (c) of which the average particle size is 30 to 150μm.

10. A high toughness ceramic as set forth in any preceding claim, wherein the phase (a) comprises an oxide of aluminum, scandium, yttrium or a rare earth metal.

11. A high toughness ceramic as set forth in any preceding claim, wherein the phase (a) comprises aluminum oxide or yttriumoxide and the metal of the phase (b) is at least one element selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum and wolfram.

12. A high toughness ceramic as set forth in claim 9, wherein the phase (a) comprises yttrium oxide and the metallic element of the particle phase (b) is titanium and/or vanadium.

13. A high toughness ceramic as set forth in claim 12,

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wherein the phase (a) is present in an amount of 0.05 to 10% by volume and the particle phase (b) is present in an amount of 5 to 40% by volume.

14. A process for the preparation of a high toughness ceramic which comprises hot-pressing a mixture comprising (1) at least one metal selected from the group consisting of aluminum, scandium, yttrium and rare earth elements or a hydride, carbide, nitride, silicide or oxide thereof, (2) at least one metal selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum and wolfram or a hydride, carbide, nitride, silicide or oxide thereof having an average particle size of 5 to 100μm and (3) a silicon carbide powder having an average particle size of 0.1 to 2μm, at a temperature of 1900 to 2300°C either under vacuum or in an inert gas atmosphere.

15. A process for the preparation of a high toughness ceramic as set forth in claim 14, which comprises adding metallic yttrium and metallic titanium or/and metallic vanadium to the silicon carbide, hot-pressing the obtained mixture at 2000 to 2200°C and immediately and slowly cooling the mixture.

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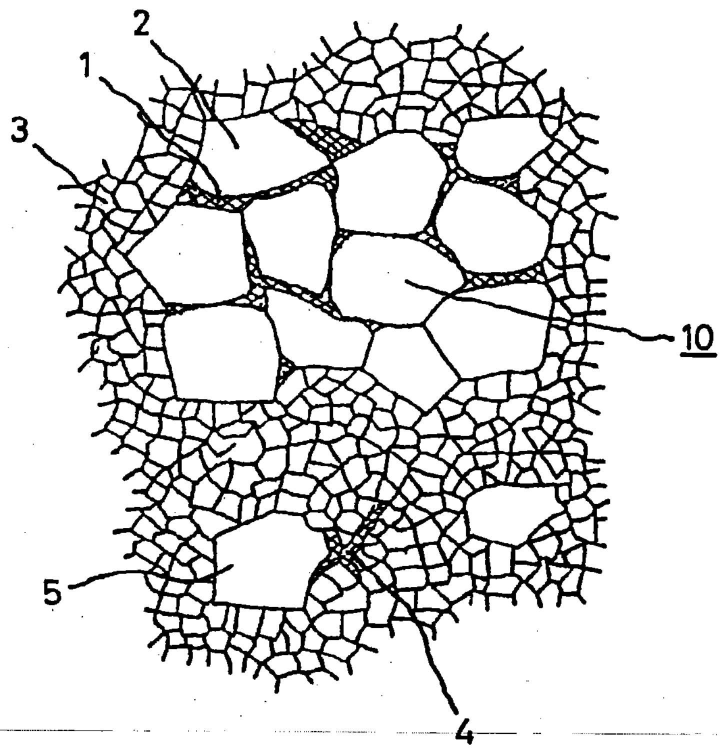

FIG. 1

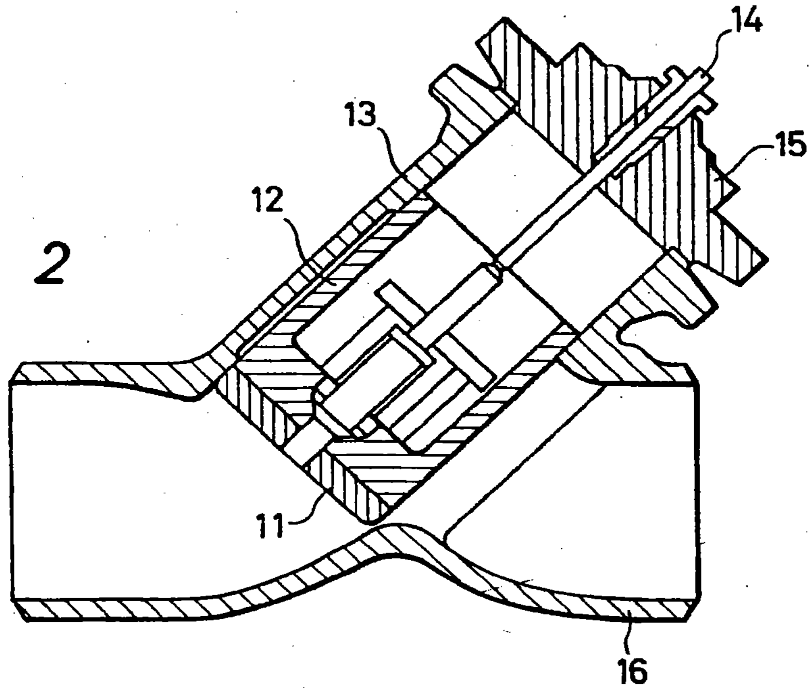

FIG. 2

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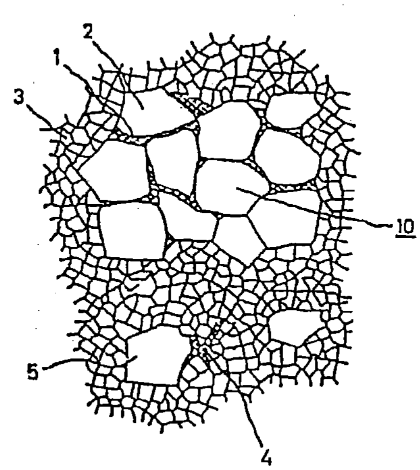
(54) **High toughness ceramics and process for the preparation thereof.**

(57) The present invention relates to a sintered product containing silicon carbide as a main component which comprises a phase (a) (1) (4), containing at least one metal selected from among A1, Sc, Y and rare earth elements and oxygen, a particle phase (b) (2) (5), comprising at least one metal carbide selected from among carbides of Ti, Zr, Hf, Va, Nb, Ta, W and the like, a composite particle phase (c) (10), comprising said phase (a) and said phase (b) surrounding the phase (a) and silicon carbide matrix (d) (3), in which the above phase (a) (4), (b) (5) and (c) (10) are dispersed.

The silicon carbide sintered product of the present invention exhibits a remarkably high strength and a remarkably high toughness which have not been attained up to this time, so that it can form various heat-resisant structural materials having a high reliability.

FIG. 1



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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl 4)
A	CHEMICAL ABSTRACTS, vol. 94, no. 20, May 1981, page 296, abstract no. 161473n, Columbus, Ohio, US; & JP-A-80 116 668 (ASAHI GLASS CO. LTD.) 08-09-1980 ---	1-14	C 04 B 35/56
A	CHEMICAL ABSTRACTS, vol. 84, no. 14, 5th April 1976, page 301, abstract no. 94535n, Columbus, Ohio, US; & JP-A-75 115 211 (TOYOTA CENTRAL RESEARCH AND DEVELOPMENT LABORATORIES INC.) 09-09-1975 ---	1-15	
A	CHEMICAL ABSTRACTS, vol. 99, no. 18, October 1983, page 302, abstract no. 144942a, Columbus, Ohio, US; & JP-A-58 95 650 (KYOSERA K.K.) 07-06-1983 ---	1	**TECHNICAL FIELDS SEARCHED (Int Cl 4)**
D,A	JOURNAL OF THE AMERICAN CERAMIC SOCIETY, vol. 67, no. 8, August 1984, pages 571-574, Columbus, Ohio, US; G.C. WEI et al.: "Improvements in mechanical properties in SiC by the addition of TiC particles" * Whole document * -----	1	C 04 B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	02-10-1986	SCHURMANS H.D.R.

CATEGORY OF CITED DOCUMENTS

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